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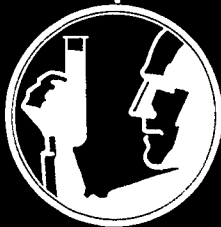
THE DEVELOPMENT OF HEAT-RESISTANT PAINTS FOR METALS

Prepared under Navy, Bureau of Naval Weapons
Contract NOW-62-0727-d

Final Report

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ABSTRACT

Studies were made to develop a protective paint that could be cured at a low temperature to produce a heat-resistant and corrosion-resistant coating on metals. A paint—consisting of a mixture of zinc oxide, dimethyl hydrogen phosphite, and an aqueous dispersion of colloidal silica—was developed that cures at normal temperatures to consistently produce coatings that are hard, well bonded, and resistant to heat, water, thermal shock, corrosion by salt spray, weathering, and many common chemicals. The availability of moisture from the environment during the early stages of curing is critical in obtaining the desired properties; the requirements have been defined.

Other paint systems that were investigated during the studies included combinations of: zinc oxide, dimethyl hydrogen phosphite, and ethyl acid phosphate; zinc oxide and dimethyl hydrogen phosphite with hydrated silica and alumina; zinc oxide with di-n-butylamine phosphate; lithia and beryllia with organo-phosphorus compounds; dimethyl hydrogen phosphite with boron glass frits containing oxides of magnesium, zinc, barium, and phosphorus; and zinc oxide and dimethyl hydrogen phosphite with several refractory-metal powders.

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THE DEVELOPMENT OF HEAT-RESISTANT PAINTS FOR METALS

I. INTRODUCTION

The objective of this research project was to develop a heat-resistant coating for metals that could be cured without baking. The major performance goals for the coating were heat stability at 1000° F for extended periods of time and protection of metals against weathering and salt-water corrosion. A durability of at least one year under normal atmospheric weathering was desired.

This research project was a continuation of the work carried out for the Bureau of Naval Weapons under Contracts NO-as-60-6075-c and NOw-61-0546-d. The work described in this report was done under Contract NOw-62-0727-d.

In studies conducted under the earlier contracts, combinations of a large number of metal oxides and ceramic frits with various liquid organo-phosphorus compounds were investigated for making coatings with the desired properties. A mixture of zinc oxide (ZnO), dimethyl hydrogen phosphite (DMHP), and ethyl acid phosphate (EAP) gave coatings on aluminum that showed attractive properties. The cured coating withstood heating at 1000° F for over 200 hours and the thermal shock of quenching in cold water from this temperature. In addition, the coatings had good adhesion to aluminum and adequate resistance to wet abrasion. However, coatings with these properties could not be produced consistently. Under this contract (NOw-62-0727-d) studies were undertaken to develop methods for the consistent preparation of ZnO-DMHP coatings with the desired properties. This objective was successfully accomplished.

In the course of this work, studies were made of the effects of the following factors on coating properties: curing conditions, additives, variations in the components, purity of the principal component (DMHP), methods of preparing and applying the coating, and condition of substrate. In addition to these studies, the reactions of zinc oxide with several organo-phosphorus compounds were studied to obtain information about the reaction of ZnO with DMHP. An extensive evaluation of the properties of the best coating developed also was carried out.

II. SUMMARY

A protective coating for metals has been developed that is hard, well bonded, and resistant to heat, to water, to thermal shock, to corrosion by salt spray, to weathering, and to attack by common organic chemicals. It is also a good electrical insulator. The coating—a mixture of zinc oxide (ZnO), dimethyl hydrogen phosphite (DMHP), and an aqueous dispersion of colloidal silica (Ludox LS)—can be cured satisfactorily without heating. The most satisfactory conditions for curing are obtained by spraying the coating intermittently with water.

The results from the various studies that were made in the development of this coating are as follows:

1. Studies were made to determine the effects of curing environment, curing time, and condition of substrate on the properties of ZnO-DMHP-Ludox LS coatings. A coating that is heat resistant and water resistant has been prepared repeatedly from a mixture of 10 parts of ZnO, 12 parts of DMHP, and 1 part of a colloidal silica dispersion (Ludox LS) by curing at 72° F and 75% RH. Similar coatings cured at other temperatures and relative humidities were either not heat resistant or not water resistant. Studies were made of the effect of curing time at 72° F and 75% RH on the properties of the coatings, and it was found that the minimum curing time under these conditions to obtain heat- and water-resistant coatings was approximately 2 hours. The remainder of the curing period did not have to be under controlled conditions. After 2 hours at 72° F and 75% RH, the weight of the coating became constant, probably due to completion of liberation of methanol. Earlier work showed that methanol is eliminated in the reaction of ZnO with DMHP. Sanding aluminum panels and rinsing them with acetone was shown to be sufficient pretreatment of panels for the production of good coatings. This is the procedure that has been used for preparing panels for all work described in this report.

2. A method was developed for the production of heat-resistant, water-resistant, ZnO-DMHP-Ludox LS coatings without the necessity of controlling the temperature and humidity of the environment during the cure. It was found that heat-resistant, water-resistant coatings were formed in a curing environment not normally satisfactory for forming good coatings, if the coatings were kept wet by spraying intermittently with water during the first 90 minutes of curing.

3. A hydrated alumina (Baymal), a hydrated silica (Hi-Sil 233), and an ultrafine pyrogenic silica (Cab-O-Sil) were evaluated in coating compositions similar to that employed in making the best coatings containing Ludox LS. These studies showed that aqueous dispersions of Baymal and Cab-O-Sil could be used in place of Ludox LS to produce coatings equivalent to those containing

Ludox LS in heat resistance, water resistance, and hardness. The Baymal coatings were slightly poorer in bonding than Ludox LS coatings, and the bonding of Cab-O-Sil coatings was considerably poorer. The substitution of Baymal for Ludox LS is of continued interest because heat-resistant, water-resistant coatings were obtained from compositions containing Baymal when they were cured at 72° F and either 60% or 75% RH; compositions containing Ludox LS must be cured at 72° F and 75% RH to obtain coatings that are both heat and water resistant.

4. Studies of coating compositions that were basically 10 parts of ZnO, 12 parts of DMHP, and 1 part of ethyl acid phosphate (EAP) showed that coatings could be produced that were either water resistant or heat resistant, depending on the relative humidity. However, both properties could not be obtained simultaneously and reproducibly by curing under any of the conditions of temperature and relative humidity that were tried.

5. Coatings prepared with commercial DMHP and coatings prepared with DMHP purified by distillation had similar properties.

6. A solution of the ZnO-DMHP-EAP coating material in DMHP was applied to aluminum panels and allowed to stand for 24 hours. Subsequent heating of the panel to drive off volatiles resulted in formation of a crust that could be removed easily. After the crust was removed, a surface coating remained on the aluminum that was coherent, heat resistant, water resistant, and fairly hard.

7. Several reactions of zinc oxide with polyphosphoric acid, with the methyl and ethyl esters of polyphosphoric acid, and with di-n-butylamine phosphate or phosphite were studied in attempts to learn more about the ZnO-DMHP reaction. The reactions of ZnO with polyphosphoric acid did not yield coatings and hence did not resemble the ZnO-DMHP reaction. Coatings were obtained from the reaction of different mole ratios of ZnO with the esters of polyphosphoric acid. However, compared to the ZnO-DMHP coatings, they were generally poor in water resistance, heat resistance, and surface appearance; and curing conditions did not affect the properties of the coatings in any identifiable pattern. These results are entirely different from those obtained with the ZnO-DMHP reaction, and thus it was concluded that the modes of coating formation for the two reactions are probably different. Coatings prepared by the reaction of ZnO and di-n-butylamine phosphite and ZnO and di-n-butylamine phosphate were similar to coatings prepared by the reaction of ZnO and DMHP. The properties of both types of coatings depended on curing conditions; and, under the same curing conditions, the properties

were similar. On the basis of the similarity in the properties of the coatings, the reactions of ZnO with di-n-butylamine phosphite or with DMHP may both proceed through the formation of phosphorous acid. In the presence of metal oxide, di-n-butylamine phosphite is known to hydrolyze to butylamine and phosphorous acid. Hydrolysis of DMHP to phosphorous acid also is possible.

8. Coatings made from mixtures of DMHP and EAP with lithia, beryllia, and various other oxides were generally inferior in properties to ZnO-DMHP-Ludox coatings. However, one coating containing beryllia and zinc oxide was about as good as the ZnO-DMHP-Ludox coating.

9. Four boron oxide frits of different composition reacted with DMHP or EAP to form coatings. One frit that contained magnesium oxide gave coatings that were similar in properties to the best coatings produced thus far and further work with this frit appears to be worth while. The coatings prepared with the other frits (the ones containing zinc, barium, or phosphorus oxide) had inferior properties.

10. Titanium, zirconium, and aluminum were evaluated as modifiers in the ZnO-DMHP coating system. It was postulated that these refractory metals might increase the heat resistance of ZnO-DMHP coatings, but only coatings with inferior properties were obtained.

III. MATERIALS AND PROCEDURES

A. Materials

The organo-phosphorus compounds used for this research were commercial-grade products obtained from the Virginia-Carolina Chemical Corporation. Ludox LS, an aqueous dispersion of 33% colloidal silica, and Baymal, a hydrated alumina, were obtained from Du Pont de Nemours and Company. Hi-Sil 233, a hydrated silica, was obtained from the Columbia Southern Chemical Corporation; and Cab-O-Sil, an ultrafine pyrogenic silica, was obtained from the Cabot Company, Incorporated. Aluminum powder was obtained from the Reynolds Aluminum Company, and titanium and zirconium powders were obtained from E. H. Sargent and Company. The aluminum for the coating substrate was Alclad 2024-T3 (Aluminum Company of America). The other chemicals used were reagent-grade products obtained from the General Chemical Division of Allied Chemical Corporation.

B. Preparation and Curing of Coatings

Coating mixtures were prepared by mixing the metal oxide with the organo-phosphorus compound for 45 to 90 seconds in a Waring Blendor. If accelerators, modifiers, water, or toluene were used in the coating, they were added last, generally during the last 15 or 20 seconds of mixing. In a few experiments, the quantities of materials available were small, and the components were mixed on a glass plate with wood or stainless-steel spatula. Work done under previous contracts has shown that there are essentially no differences in the properties of coatings formed by the two mixing techniques.

After the coating components were thoroughly mixed, the mixtures were sprayed or doctored on aluminum panels within ten minutes. Both spraying and doctoring were found in earlier studies to give coatings with similar properties, as long as the coating mixture was not too thick. After application to the panels, the coatings were cured in one of three ways: (1) they were cured under prevailing laboratory conditions of temperature and relative humidity; (2) they were cured at controlled temperature and relative humidity; or (3) they were kept wet for 90 minutes by intermittent spraying with water, and then cured for 24 hours under prevailing laboratory conditions. Normally, the coatings were cured a minimum of 24 hours before being evaluated. The curing techniques used for preparing specific samples are given in the sections in which the samples are discussed.

C. Coating Evaluation Procedures

1. Screening evaluation

After application to the aluminum substrate and curing, the coatings were evaluated for appearance, hardness, bonding, water resistance, and heat resistance. Hardness was determined by scratching the coating with a fingernail. Bonding was evaluated by bending a coated panel over a conical mandrel (maximum diameter of bend 0.5 in.) and observing the loss of adhesion of the coating at the bend. Water resistance was determined by rubbing the wet coating with a wet paper towel and observing any loss of adhesion to the panel. Heat resistance was determined by placing the coated panel (coated side up) on a laboratory hot plate at 1000° F for 5 minutes, then quenching it in cold water and observing the effect on the coating.

A rating system similar to the one outlined in the final report on Contract NOas-60-6075-c (February 3, 1961) was used to indicate the performance of coatings. In this system, numbers from 1 to 4 are used to indicate the performance of coatings as follows:

Hardness

- Rating 1 - very hard, cannot be scratched by a fingernail
- Rating 2 - hard, can be scratched by a fingernail if moderate pressure is applied
- Rating 3 - soft, can be easily scratched by a fingernail
- Rating 4 - very soft, can be rubbed off the panel with finger

Surface appearance of coating after curing at room temperature

- Rating 1 - smooth, even surface
- Rating 2 - rough, uneven surface

Bonding

- Rating 1 - good bonding, no loss of coating on bending panel over a 0.5-in. diameter mandrel
- Rating 2 - fair bonding, very slight damage at unprotected edges of panel on bending over a 0.5-in. diameter mandrel
- Rating 3 - poor bonding, considerable loss of coating on bending panel over a 0.5-in. diameter mandrel

Water resistance (wet abrasion method)

- Rating 1 - insoluble and tightly adhered to panel
- Rating 2 - insoluble but only partially adhered to panel
- Rating 3 - soluble, not adhered to panel

Heat resistance—1000° F for 5 minutes plus quenching

- Rating 1 - not damaged
- Rating 2 - very slightly damaged at unprotected edges
- Rating 3 - badly damaged, coating flaked off or foamed

2. Detailed evaluation

a. Salt-spray corrosion resistance

The salt-spray corrosion resistance of coated panels was determined according to Specification TT-P-141, Method 6061, MIL-P-14105 (CE).

The edges of the coated panels to be evaluated were sealed by dipping them to a depth of 0.1 inch in melted paraffin, and then the panels were placed in wooden blocks inside a salt spray cabinet (Type CA, Salt Fog Test Cabinet - Industrial Filter and Pump Manufacturing Company, Chicago). The

blocks were slotted so that the panels were supported at an angle 30° from the vertical. A 20% aqueous sodium chloride solution having a pH of 6.5 to 7.2 was used as the salt spray. The temperature of the salt-spray cabinet was kept at 95[±] 2° F throughout the exposures, and the air pressure to the spray nozzles was maintained at 10-12 psi. Panels were removed from the cabinet after exposures of 24, 48, 72, 100, and 150 hours; rinsed thoroughly with tap water; drained; and allowed to dry. The dry panels were evaluated visually for corrosion.

b. Accelerated-weather resistance

An Atlas-Twin Arc Weather-Ometer was used for accelerated weathering of the coatings. The Weather-Ometer was operated at approximately 100° F, and coated panels were sprayed with water for 9 minutes during each hour of exposure. The panels were exposed for a total of 300 hours. At intervals throughout the exposure, they were inspected visually for signs of failure.

c. Thermal-shock resistance

To determine the thermal-shock resistance of coatings, coated panels were heated on a laboratory hot plate at 1000° F for approximately 5 minutes, then quenched in tap water. The heating and cooling cycle was repeated until the coating showed signs of flaking or chipping or at least 10 cycles were completed.

d. Chemical resistance

The chemical resistance of coatings was determined by immersing coated panels in the following liquids for 18 hours at 25° C: distilled water, mineral spirits, 0.01 N HCl, 0.1 N HCl, 0.01 N NaOH, 0.1 N NaOH, methyl ethyl ketone, benzene, toluene, nitrobenzene, ethyl acetate, ether, and 3.5% aqueous sodium chloride solution. After immersion, the coated panels were examined for failures.

e. Shear-bond strength

Shear-bond strength was used as an indication of the strength of the bond between a coating and a metal substrate.

Two panels were coated with the coating mixture, and the coated surfaces were pressed together. The sample was cured overnight at room temperature and then heated at 250° F for 2 hours. Heating was necessary to complete the cure. The cured sample was placed in an Instron Tester, and

load was applied to the sample in the shear direction at a rate of 0.2 inch per minute until the bond broke. The load applied at the break point was taken as the shear bond strength.

f. Dielectric strength

The dielectric strength of a coating was determined by placing a coated panel between two 0.25 in. diameter flat electrodes and determining the voltage at which electrical breakdown occurred. This voltage divided by the coating thickness in mils is reported as the dielectric strength.

g. Electrical resistance

The electrical resistance was measured with a flat circular electrode 1.125 in. in diameter and weighted to apply a pressure of 2 lb/in.². The electrode was placed on a coating, and the resistance between the electrode and the metal panel on which the coating was applied was measured. A modified Wheatstone bridge was used for determining the resistance. Results are reported in ohms per square inch per mil (ohms/in.²/mil).

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Coatings Prepared from Zinc Oxide (ZnO), Dimethyl Hydrogen Phosphite (DMHP), and Ethyl Acid Phosphate (EAP)

1. Effects of curing temperature and relative humidity on coating properties

Experiments were conducted to study the effects of temperature and relative humidity during curing on the properties of ZnO-DMHP-EAP mixtures. During the previous contract period, experiments were conducted at curing conditions of 136° F and relative humidities ranging from 20 to 70%. Experiments at 60°, 72°, and 100° F and different relative humidities were made during this contract period.

The coatings evaluated were basically 10 parts of ZnO, 12 parts of DMHP, and 1 part of EAP. Varying amounts of distilled water were added to some of the mixtures. The mixtures were prepared and coated on aluminum panels as described in Section III, and the coated panels were cured for 24 hours in a controlled environment. Data on curing conditions and coating properties are given in Table I.

Table I. Effects of Curing Temperature and Relative Humidity on Water and Heat Resistance of ZnO-DMHP-EAP Coatings

Coating composition, parts by weight ^a			Curing conditions ^b		Ratings of cured coatings	
ZnO	DMHP	EAP	Relative humidity, %	Temperature, °F	Water resistance	Heat resistance
10	12	1	90	60	3	1
10	12	1	99	60	3	1
10	12	1	35	72	3	1
10	12	1	60	72	3	1
10	12	1	65	72	3	1
10	12	1	75	72	3	2
10	12	1	75	72	3	1
10	12	1	75	72	1	2
10	12	1	80	72	3	3
10	12	1	20	100	3	1
10	12	1	28	100	3	1
10	12	1	50	100	3	1
10	12	1	55	100	3	3
10	12	1	57	100	1	2
10	12	1				
10	12	1	35	72	3	1
10	12	1	60	72	3	1
10	12	1	35	72	3	1
10	12	1	60	72	3	1
10	12	1	65	72	3	1
10	12	1	65	72	3	2
10	12	1	65	72	3	3
10	12	1	65	72	2	2
10	12	1	65	72	3	1
10	12	1	75	72	2	1
10	12	1	75	72	1	2
10	12	1	75	72	3	2
10	12	1	75	72	3	3
10	12	1	75	72	1	3
10	12	1	20	100	3	1
10	12	1	28	100	3	1
10	12	1	50	100	3	1
10	12	1	57	100	1	3
10	12	1	57	100	1	2

^aDMHP=dimethyl hydrogen phosphite; EAP=ethyl acid phosphate

^bCoatings were cured 24 hours

At 100° F, a critical relative humidity of about 55% was found. Coatings cured above this critical relative humidity were water resistant but not heat resistant; coatings cured below this critical relative humidity were heat resistant but not water resistant. At 136° F, the similar critical relative humidity was found earlier to be about 38%.

No such critical relative humidity was found for curing ZnO-DMHP-EAP coatings at 60° or 72° F. Coatings cured at 72° F and 65%, or less, relative humidity were heat resistant but not water resistant (Table I). Erratic results were obtained on coatings cured at 75% relative humidity. In one trial, the coating was heat resistant; in another trial, the coating was water resistant; and in a third trial, the coating was neither heat resistant nor water resistant. The coatings cured at 72° F and 80% relative humidity were neither heat nor water resistant. No explanation for this behavior is known.

The ZnO-DMHP-EAP coatings cured at 60° F and 90 or 99% relative humidity were usually heat resistant but not water resistant. Some representative data showing these results are also given in Table I.

Coatings prepared from the mixture described above and containing 1 or 4 parts of water were also cured at various temperatures and relative humidities. No differences were found in the properties of these coatings cured at 136° or 100° F and the coatings that did not contain water. At a curing temperature of 72° F, the only difference noted was that erratic results were obtained at 65% relative humidity; however, the data are not conclusive.

These data indicate a general correlation between the relative humidity and temperature for curing and the properties developed in ZnO-DMHP-EAP coatings. As the curing temperature is increased, the permissible maximum relative humidity for obtaining heat resistance is decreased from about 100% at 60° F to 38% at 136° F. The production of water resistance in the coatings also appears to follow a trend; but, to obtain water resistance, curing should be carried out above certain values of relative humidity that decrease with increasing temperature. It appears, however, that no relatively broad band of curing temperature and relative humidity exists where satisfactory coatings can be made.

The opposing humidity requirements for obtaining both water and heat resistance probably explain why it has been so difficult to obtain both properties in a single coating. Presumably, the coatings that have shown excellent stability to both heat and water were prepared under chance combinations of conditions that were favorable.

2. Effect of curing time on coating properties

The heat resistance and water resistance were determined for coatings similar to those described above that were cured at 100° F and 20 or 50% relative humidity for 2 hours and for 24 hours. The results given in Table II show that all of these coatings had good heat resistance but poor water resistance.

3. Effect of purity of DMHP on coating properties

It was thought that impurities present in commercially supplied DMHP might be the cause of some of the inconsistencies in properties obtained with the ZnO-DMHP-EAP coatings. Coatings prepared from the following formulations were evaluated to compare distilled and undistilled DMHP:

- (1) 10 parts of ZnO, 12 parts of DMHP
- (2) 10 parts of ZnO, 12 parts of DMHP, 1 part EAP
- (3) 10 parts of ZnO, 12 parts of DMHP, 1 part water

The DMHP was fractionally distilled under a nitrogen atmosphere at 17 mm pressure, and the fraction boiling between 68. 5° C and 70° C was collected and used in this series of trials. This fraction represented 95% of the original charge.

The coatings prepared with the distilled DMHP did not differ in heat resistance or water resistance from the coatings prepared with undistilled DMHP.

4. Evaluation of DMHP as a solvent for the ZnO-DMHP-EAP coating

It had been postulated in the earlier studies that the coatings prepared from ZnO, DMHP, and EAP consisted of a polymeric material, which served as a binder, and of unreacted ZnO. If the polymeric material could be dissolved in a solvent and applied to metals, the problems of application and curing might be overcome. Previous attempts to find a solvent for the coatings were unsuccessful, but during this contract period it was found that coatings heated to 1000° F for 5 minutes could be dissolved in an excess of DMHP. The heated coatings were water resistant.

A number of panels that had been coated with a ZnO-DMHP-EAP formulation were immersed in DMHP overnight. The coatings dissolved completely. Approximately 75% of the DMHP was distilled from the solution under reduced pressure, and the residue was applied to aluminum panels.

Table II. Effect of Curing Time on Water and Heat Resistance of ZnO-DMHP-EAP Coatings Cured at 100°F and Different Relative Humidities

Coating composition, parts by weight ^a				Curing conditions			Ratings of cured coatings	
ZnO	DMHP	EAP	Water	Relative humidity, %	Temperature, °F	Time, hr	Water resistance	Heat resistance
10	12	1	-	50	100	2	3	1
10	12	1	-	50	100	24	3	1
10	12	1	1	50	100	2	3	1
10	12	1	1	50	100	24	3	1
10	12	1	-	20	100	2	3	1
10	12	1	-	20	100	24	3	1
10	12	1	4	20	100	2	3	1
10	12	1	4	20	100	24	3	1

^aDMHP = dimethyl hydrogen phosphite; EAP = ethyl acid phosphate

After 24 hours at room temperature, the coatings were not dry, presumably because of the low volatility of the DMHP. However, when the panels were heated on a hot plate to 1000° F, a crusty, brittle solid remained on the panels. Most of this solid material came off when a panel was placed in water; but a thin coating that was heat resistant, hard, water resistant, and well bonded to the aluminum was left on the panel. It was not determined whether a separate coating was deposited on the surface of the aluminum panel or whether the surface of the panel was converted to a complex aluminum-phosphorus-oxygen salt.

5. Nature of bonding of zinc in ZnO-DMHP-EAP coatings

In attempts to obtain information that would lead to the production of heat- and water-resistant coatings, studies were made of the nature of the bonding of the zinc in ZnO-DMHP-EAP coatings that were not water resistant and in those coatings that were water resistant.

Samples of both types of coatings were prepared by casting the basic ZnO-DMHP-EAP formulation on glass plates and curing them at 100° F under the proper humidity conditions. The coatings were scraped from the plates, weighed, and suspended separately in water heated to 60° C for several hours. The mixtures were then filtered, and the residues were washed several times with distilled water, dried, and weighed.

Both the water-resistant and the nonwater-resistant coatings were found to be partially soluble in water. About 41% of the coating that was not water resistant was soluble, and about 17% of the coating that was water resistant was soluble.

Sodium ferrocyanide was added to the filtrates and zinc ferrocyanide precipitated. Approximately 2.7 times more precipitate was obtained from the filtrate of the coating that was not water resistant than from the filtrate of the water-resistant coating. This difference in the amounts of zinc ferrocyanide precipitate from the two types of coatings agrees with the difference in the solubilities of the coatings, as would be expected. These results indicate that the zinc present in the water-soluble fractions of the coatings was present as ions or in some form that was easily ionized when dissolved in water.

The insoluble residue from the water-resistant coating was suspended in a 10% aqueous calcium chloride solution, and the suspension was heated at near boiling for several hours, while being stirred, and then it was allowed to stand for 7 days. The suspension was filtered and the residue was washed several times with distilled water and then dried. Spectrographic analysis of the residue showed that it contained only 0.1% calcium. If the zinc present in the insoluble residue of the water-resistant coating was present as easily replaceable ions, the coating should have contained more calcium.

B. Coatings Prepared from ZnO, DMHP, and Ludox LS

Earlier studies under Contract NOW-61-0456-d yielded promising results with ZnO-DMHP coatings containing colloidal silica that made these coatings of interest for further study.

1. Effects of curing temperature and relative humidity on coating properties

In continuing the study of coatings prepared from ZnO, DMHP, and colloidal silica, coatings on aluminum panels were prepared from a mixture of 10 parts of ZnO, 12 parts of DMHP, and 1 part of Ludox LS (an aqueous dispersion of colloidal silica containing 33% solids) and cured at 60°, 72°, 100°, and 136° F and various relative humidities. Data on the properties of the coatings are given in Table III.

Coatings that were cured at 136° F and above a relative humidity of about 40% were water resistant but not heat resistant, while coatings cured at a lower relative humidity were heat resistant but not water resistant. A similar relationship was found at 100° F; at this temperature the critical humidity was about 56%.

A different curing pattern was observed for ZnO-DMHP-Ludox LS coatings cured at 72° F. Coatings cured at 65% relative humidity or below were neither heat resistant nor water resistant; coatings cured at 75% relative humidity were both heat resistant and water resistant; and coatings cured at 80% relative humidity were water resistant but not heat resistant. The ability to produce coatings that were both heat and water resistant by curing at 72° F and 75% relative humidity was checked repeatedly. In twelve different trials in which the ZnO-DMHP-Ludox LS coatings were cured at 72° F and 75% relative humidity, ten coatings were both heat resistant and water resistant and the other two were water resistant and had marginal heat resistance.

Coatings of this type that were cured at 60° F and at relative humidities of 90 to 99% were heat resistant but not water resistant.

Table III. Properties of ZnO-DMHP-Ludox LS Coatings Cured Under Various Conditions of Temperature and Relative Humidity^a

Relative humidity, %	Curing conditions ^b Temperature, °F	Hardness	Ratings of cured coatings		
			Bonding	Water resistance	Heat resistance
90	60	1	1	3	1
99	60	3	3	3	1
35	72	3	1	3	3
60	72	1	2	3	3
65	72	1	1	3	3
75	72	1	1	1	1
80	72	1	1	1	3
20	100	1	1	3	1
55	100	1	1	3	1
57	100	1	2	1	3
38	136	3	1	3	1
43	136	1	2	1	2
49	136	1	3	1	3

^aCoatings prepared from a mixture of 10 parts of ZnO, 12 parts of DMHP, and 1 part of Ludox LS.

^bCoatings cured 24 hours

These results show that the curing conditions that produce a coating that is both water resistant and heat resistant are apparently quite specific.

2. Effect of curing time on coating properties

a. Curing time at 72° F and 75% relative humidity

As shown above, heat-resistant, water-resistant, hard, well-bonded coatings can be prepared from a mixture of 10 parts of zinc oxide, 12 parts of DMHP, and 1 part of Ludox LS by curing under the specific conditions of 72° F and 75% relative humidity for 24 hours. Further studies were conducted to determine whether the coatings had to be cured the entire 24 hours under these optimum conditions.

Five aluminum panels that were coated with a formulation containing 10 parts of zinc oxide, 12 parts of DMHP, and 1 part of Ludox LS were cured for 24 hours and then evaluated. Four of the coated panels were cured at 72° F and 75% relative humidity for 0. 5, 1, 2, and 24 hours; and then they were cured for the remainder of the 24-hour curing period under ambient laboratory conditions, which were 72° F and 55% relative humidity. As a control, one of the coated panels was cured for 24 hours under the ambient conditions. Data on the properties of the coatings are shown in Table IV.

Table IV. Properties of Zinc Oxide-DMHP-Ludox LS Coatings Cured at 72° F and 75% Relative Humidity for Varying Times

Curing time, hours		Coating properties	
At 72° F, 75% RH	At 72° F, 55% RH	Water resistance	Heat resistance
0	24	3	1
0. 5	23. 5	3	1
1	23	2	1
2	22	1	1
24	0	1	1

The data indicate that about 2 hours under optimum curing conditions is sufficient to give heat- and water-resistant coatings.

b. Weight loss during curing

The weight loss of a ZnO-DMHP-Ludox LS coating during curing was followed to determine how the rate of weight loss varied with time and how long was required for a coating to reach weight equilibrium.

A coating mixture was prepared, as in previous studies, from 10 parts of ZnO, 12 parts of DMHP, and 1 part of Ludox LS. The mix was coated on a preweighed aluminum panel within 2 minutes after mixing, and the coated panel was placed on an analytical balance so the weight loss could be followed during curing. All of these operations were carried out in air at 72° F and 57% relative humidity; hence, the coating formed was heat resistant but not water resistant.

Figure 1 shows a curve of coating weight versus time. No significant fluctuations occurred in the rate of weight loss during drying to indicate a step-wise reaction. The weight of the coating reached a constant value in approximately 90 minutes.

Theoretically, assuming complete hydrolysis of the DMHP to methanol and making allowance for the water added in the Ludox, there could be a maximum of about 35% volatiles as methanol and water. The weight lost by the coating in the reaction carried out on the analytical balance was approximately 37%. This would indicate that the DMHP is quantitatively hydrolyzed.

It was noted above that the time required for the same type coating to cure under optimum conditions was also about 2 hours. These data together indicate that the reactions that ultimately determine the properties of a coating take place early in the curing period, and that the reaction also results in the elimination of one or more volatile components. If the basic DMHP-ZnO reaction involved hydrolysis of the DMHP to phosphorous acid, as indicated by the results of the studies given in a later section (Section IV-C), methyl alcohol and water would be formed. Both of the materials have been detected by analysis of the volatiles from the zinc oxide-DMHP reaction.

3. Effect of keeping coating surface wet during curing on coating properties

For the zinc oxide-DMHP-Ludox LS coating to be practical, methods had to be found for curing that do not require environmental control. Since this coating can be cured at about normal room temperature (72° F) at a fairly high relative humidity (75%), experiments were made to determine whether curing could be accomplished by keeping the surface of the coating wet.

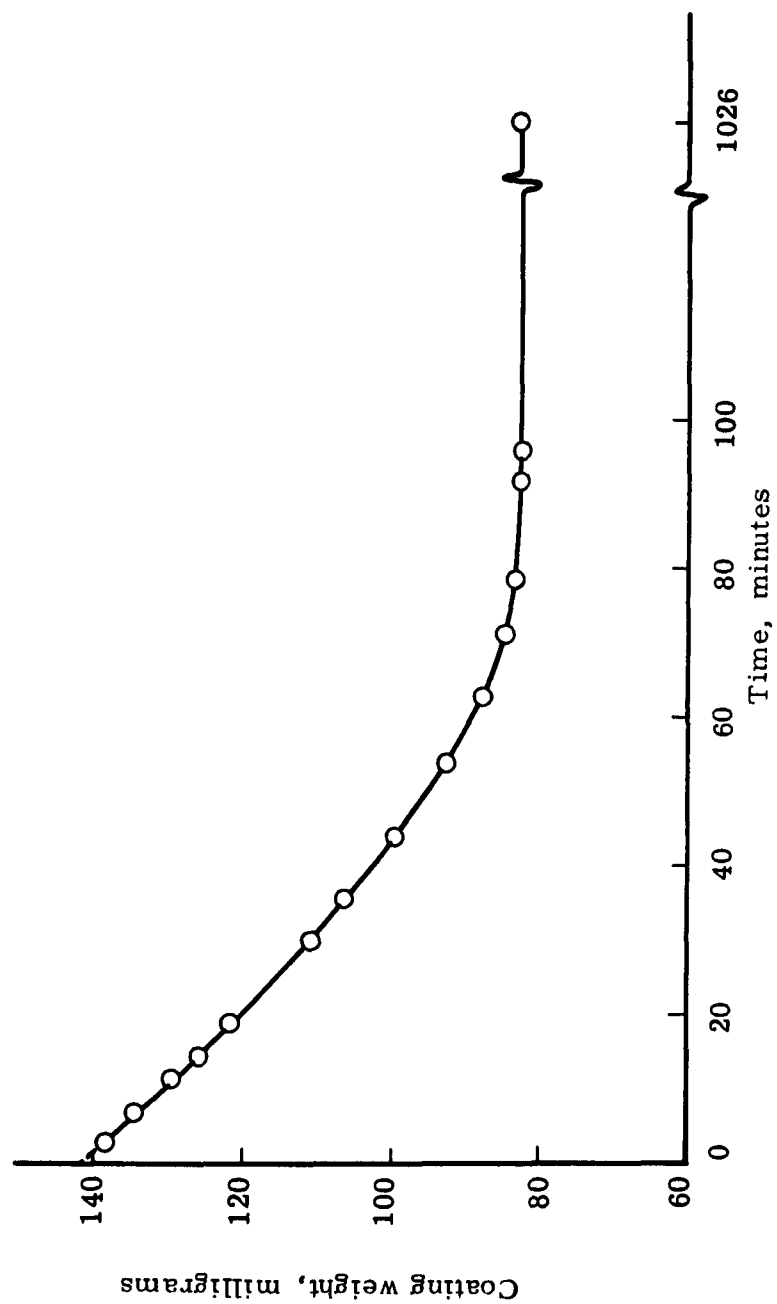


Figure 1. Weight-Time Curve During Curing of a ZnO-DMHP-Ludox LS Coating at 72° F and 57% Relative Humidity.

Coatings on aluminum panels that were prepared from a mixture of 10 parts of zinc oxide, 12 parts of DMHP, and 1 part of Ludox LS were sprayed with a fine mist of water at 5-minute intervals for a total of 90 minutes, starting immediately after application. Then they were allowed to stand under prevailing laboratory conditions for 24 hours. During the experiments, the temperature in the laboratory ranged from 68° to 84° F, and the relative humidity ranged from 42 to 69%. For comparison, duplicate coatings prepared at the same time but not sprayed were allowed to stand in the laboratory during the same curing period. In six different trials, five of the coatings that were sprayed were both heat resistant and water resistant, and the other coating was water resistant but not heat resistant. All of the sprayed coatings were hard, were well bonded to the aluminum, and with one exception, had good appearances. The control coatings that were not sprayed were heat resistant but none was water resistant.

The experiments described above were repeated with a coating composed of 10 parts of zinc oxide, 12 parts of DMHP, and 1 part of EAP. Of the sprayed coatings, three were both heat resistant and water resistant, and three were heat resistant but not water resistant. All of these sprayed coatings also were hard, had good appearances, and were well bonded to the aluminum. The control coatings that were not sprayed were heat resistant but not water resistant.

On the basis of the results discussed above, which are summarized in Table V, it was concluded that this technique for controlling the cure of the zinc oxide-DMHP-Ludox coating was a good practical approach to the curing problem and was worth more detailed investigation. Studies were therefore undertaken to determine the effects of variables in the "wetting" operation on the properties of the cured coatings. The variables investigated were: (a) the time interval between applying the coating and initial spraying, (b) the time interval between successive sprayings, and (c) the total time of spraying.

a. Time interval between coating and initial spraying

Coatings that were sprayed within 2 to 5 minutes after application to aluminum panels were heat resistant, water resistant, hard, and well bonded; but coatings that were not sprayed until 10 or more minutes after application to the panels were generally not water resistant.

b. Time interval between successive sprayings

After the initial spraying, which was started between 2 and 5 minutes after application of the coatings to the aluminum panels, the time interval between subsequent sprayings was varied. Coatings were sprayed

Table V. Properties of ZnO-DMHP Coatings that were Water Sprayed During Curing

Coating	Method of application of coating	Properties of coatings			
		Hardness	Surface	Bonding	Heat resistance
ZnO-DMHP-Ludox LS	doctor blade	1	1	1	1
	doctor blade	1	1	3	1
	doctor blade	1	1	1	2
	spray	1	1	1	1
	spray	1	1	1	1
	spray	1	1	1	1
	doctor blade	1	1	1	1
	doctor blade	1	1	2	1
	doctor blade	1	1	1	1
ZnO-DMHP-EAP	spray	1	1	1	1
	spray	1	1	2	1
	spray	1	1	1	1
	doctor blade	1	1	1	1
	doctor blade	1	1	1	1
	doctor blade	1	1	1	1
	spray	1	1	1	1
	spray	1	1	1	1
	spray	1	1	3	1

at 2-, 5-, and 10-minute intervals. Heat- and water-resistant coatings were obtained most consistently when spraying was done at 5-minute intervals. Coatings sprayed at 2-minute intervals were often both heat and water resistant, but sometimes they were slightly lacking in water resistance. Coatings sprayed at 7- or 10-minute intervals were poor in water resistance.

c. Total time of spraying

To determine the total time spraying had to be continued to obtain heat- and water-resistant coatings, coatings were sprayed intermittently over periods of 30, 60, 120, and 240 minutes. The time between application of the coatings to aluminum panels and initial spraying was between 2 and 5 minutes and the fogging interval was 5 minutes. Coatings were more consistently heat resistant and water resistant when spraying was continued for 240 minutes, although, in one case, a good coating was obtained by spraying over a total time of only 30 minutes.

d. Conclusions

Although the above studies demonstrated that ZnO-DMHP-Ludox LS coatings with the desired properties can be produced consistently with the spraying technique of curing, the technique has two serious disadvantages: the coating has to be sprayed with water within 5 minutes after being applied to the substrate, and the coating has to be sprayed at rather definite intervals for a prolonged period of time. It may be possible to overcome these problems by keeping the coating moist continuously, for example, by covering the coating with a wet cloth and keeping the cloth wet throughout the curing period; and this possibility should be investigated if further work is done on these types of coatings.

4. Condition of substrate on coating properties

It is known that the condition of the substrate often affects the properties of coatings. A study was undertaken to determine the effects of various methods of preparing the aluminum panels (Alclad 2024-T3) on the properties of cured coatings. Panels were prepared for coating in the following five ways:

Panels were merely washed with acetone to remove grease.

Panels were sanded lightly to remove any oxide from the surface and then washed with acetone. This is the method that has generally been used. It produces a rougher surface than the other methods which should improve the adhesion of coatings.

Panels were soaked in DMHP. Earlier in this report (p. 11), experiments were described in which heat-resistant, water-resistant coatings were dissolved in DMHP and recoated on panels. Removal

of the hard crust formed by heating the coated panels exposed a panel surface which had obviously been modified. This exposed surface was not affected by heating to 1000° F, or by wet or dry abrasion. Subsequent investigation during this report period determined that a similar surface could be produced by soaking an aluminum panel in DMHP for periods of 8 hours or longer. It is known that pretreating of substrates will often result in better bonding of coatings; therefore, panels were pretreated in this manner for coating studies.

Panels were ground from 0.032-in. to 0.025-in. thickness and washed with acetone. The aluminum panels used in this study consisted of a core aluminum alloy overcoated with a second aluminum alloy. The overcoated alloy was removed to determine if different properties were obtained in coatings on the core alloy.

Panels were ground from 0.032 in. to 0.025 in. and wire-brushed to obtain a rough surface.

The panels prepared in these various ways were coated with a mixture of 10 parts of ZnO, 12 parts of DMHP, and 1 part of Ludox LS and cured at 72° F and 75% relative humidity. The properties of the coatings on the various panels are listed in Table VI. All the coatings had satisfactory properties except those applied to panels which were merely washed with acetone. These data indicate that sanding the panels and washing them with acetone is sufficient preparation for coating. This had been our practice in previous work and it was continued for the rest of the program.

Table VI. Properties of ZnO-DMHP-Ludox LS Coatings on Panels Treated in Various Ways

Treatment of panel ^b	Properties of coatings ^a				
	Hardness	Surface	Bonding	Water resistance	Heat resistance
Washed	2	1	3	3	3
Sanded and washed	1	1	1	1	1
Soaked in DMHP	1	1	1	1	1
Ground and washed	1	1	1	1	1
Ground, wire-brushed and washed	1	1	1	1	1

^a Coatings prepared from 10 parts of ZnO, 12 parts of DMHP, and 1 part of Ludox LS.

^b All washes were with acetone.

5. Evaluation of materials similar to Ludox LS

In this section of the report, it has been shown that substitution of Ludox LS (aqueous colloidal silica) for EAP in the ZnO-DMHP-EAP coating results in improvements in the heat resistance and water resistance of coatings. A study was conducted to determine if this improvement was specific for the aqueous colloidal silica or if it could also be obtained with similar materials. Three materials, Baymal, Hi-Sil 233, and Cab-O-Sil, which, like the colloidal silica, are hydrophilic and have large surface areas, were evaluated. Baymal is a hydrated alumina, Hi-Sil 233 is a hydrated silica, and Cab-O-Sil is an ultrafine pyrogenic silica.

The most promising coating containing Ludox LS was obtained with a mixture of 10 parts of zinc oxide, 12 parts of DMHP, and 1 part of the Ludox LS. One part of Ludox LS corresponds to 0.33 part of silica and 0.67 part of water. In a series of experiments, the following mixtures were used: 10 parts of zinc oxide, 12 parts of DMHP, 0.33 or 0.67 part of the material under consideration, and 0.67 or 0.33 part water. To determine whether water was necessary, a series of coatings was prepared in which no water was added. The aluminum panels were coated with the mixtures in the usual manner; and the coatings were cured at 72° F and 60, 75, or 90% relative humidity for 24 hours. The compositions of the coating mixtures and the properties of the coatings are given in Table VII, together with similar data on the properties of coatings containing Ludox LS.

Only the two coatings containing 0.33 part of Baymal and 0.67 part of water that were cured at 60 or 75% relative humidity and the one coating containing 0.67 part Cab-O-Sil and 0.33 part water and cured at 75% relative humidity were both heat and water resistant. These two Baymal coatings were equivalent to Ludox LS coatings in hardness, surface appearance, heat resistance, and water resistance; but bonding was slightly poorer. The Cab-O-Sil that was heat resistant and water resistant was also hard and smooth, but it was very poorly bonded.

Table VII. Properties of ZnO-DMHP Coatings Containing Materials Similar to Ludox LS

Ludox LS	Coating composition, parts by weight ^a			Curing conditions ^b Relative humidity, %	Ratings after curing				
	Baymal	Cab-O-Sil	Hi-Sil 233		Water	Hardness	Ratings after curing		
							Surface	Bonding	Water resistance
1				60	1	1	2	3	3
1				75	1	1	1	1	1
1				80	1	1	1	1	3
	0.33	-	-	60	1	1	2	1	1
	0.33	-	-	75	1	1	2	1	1
	0.33	-	-	90	3	1	3	3	1
	0.67	-	-	60	1	1	3	1	3
	0.67	-	-	75	1	1	3	3	3
	0.67	-	-	90	3	1	3	3	2
	0.67	-	-	60	1	1	3	1	3
	0.67	-	-	75	1	1	1	1	2
	0.67	-	-	90	3	1	3	3	2
	-	0.33	-	60	1	1	2	1	3
	-	0.33	-	75	1	1	1	1	3
	-	0.33	-	90	3	1	3	3	1
	-	0.67	-	60	1	1	2	2	3
	-	0.67	-	75	1	2	3	1	1
	-	0.67	-	90	3	1	2	3	1
	-	0.67	-	60	1	1	3	3	3
	-	0.67	-	75	1	1	3	3	3
	-	0.67	-	90	3	1	3	3	2
	-	-	0.67	60	3	1	2	2	1
	-	-	0.67	75	1	2	3	1	3
	-	-	0.67	90	3	1	2	3	1
	-	-	-	60	1	1	2	2	3
	-	-	-	75	1	1	3	1	2
	-	-	-	90	3	1	3	3	2
	-	-	0.67	60	3	1	2	2	1
	-	-	0.67	75	1	2	3	1	3
	-	-	0.67	90	3	1	2	3	1
	-	-	-	60	1	1	2	2	3
	-	-	-	75	1	1	3	1	2
	-	-	-	90	3	1	3	3	2

^aAll coatings contain 10 parts of zinc oxide and 12 parts of DMHP

^bAll coatings cured at 72°F and indicated relative humidity for 24 hours

This study shows that certain finely divided, hydrophilic materials other than Ludox LS can influence the formation of heat-resistant, water-resistant coatings from zinc oxide and DMHP. These materials may affect the availability of water, thus controlling the rate of hydrolysis of the DMHP and its reaction with zinc oxide. Further evaluations of Baymal appear worth while because the production of heat-resistant, water-resistant coatings from compositions containing Baymal appears to be somewhat less sensitive to the relative humidity during curing than with compositions containing Ludox LS. It is not obvious to us why Hi-Sil 233 was poorer than Baymal or Cab-O-Sil in the coating compositions, for the Hi-Sil is also a finely divided hydrophilic material.

6. Detailed evaluation of ZnO-DMHP-Ludox LS coatings

The best coating system developed in this work was a mixture of 10 parts of ZnO, 12 parts of DMHP, and 1 part of Ludox LS. In screening studies, it was found that coatings of this type, when properly cured, were heat resistant, water resistant, hard, smooth, and well bonded to the substrate. Several additional properties of this best coating system are discussed below. The coatings evaluated were applied to aluminum panels, and within 2-5 minutes after application, they were sprayed with a fine mist of water at 5-minute intervals during a total time of 90 minutes. The coatings were between 0.8 and 1.3 mils thick in single coats and between 2.0 and 2.3 mils thick in double coats.

a. Salt-spray-corrosion resistance

Coatings applied to both aluminum and easily corroded steel substrates were subjected to a salt spray in accordance with Method 6061, MIL-P-14105 (CE), Specification TT-P-141. Coatings exposed for 100 hours were in the same condition as before exposure. In addition, the protected metal substrates showed no sign of corrosion.

b. Accelerated-weather resistance

Coatings were placed in the Atlas Weather-Ometer for 300 hours. Exposure for 300 hours in the Weather-Ometer is frequently considered to be equivalent to 1 year of normal weathering. After 300 hours of exposure, the coatings showed no signs of loss of adhesion, flaking, or other visible degradation.

c. Thermal-shock resistance

Coated panels were heated to 1000°F for approximately 5 minutes and then plunged into cold water. Coated panels have been exposed to as many as 30 quenching cycles with no evidence of chipping, flaking, or loss of adhesion.

d. Chemical resistance

Coated panels were immersed in distilled water, mineral spirits, methyl ethyl ketone, benzene, toluene, nitrobenzene, ethyl acetate, or ether for 18 hours at room temperature. The coatings were not damaged in any visible manner by these solvents. However, the coatings were destroyed shortly after immersion in 0.01 N NaOH or 0.1 N HCl.

e. Shear-bond strength

The ZnO-DMHP-Ludox LS mixture did not cure at room temperature when attempts were made to bond two aluminum panels together. However, if the coated panels were cured in contact with each other overnight at room temperature, then heated to 250°C for 2 hours, the shear strength of the bond developed was found to be 140 lb/in.²

f. Dielectric strength

The dielectric strength of the coating was determined to be approximately 125 volts/mil.

g. Electrical resistance

The electrical resistance of the coating was determined to be 2.9×10^9 ohms/in.²/mil.

h. Toxicity of DMHP

It is reported in Monsanto Technical Data Sheet No. 600, dated August 22, 1957, that animal toxicity studies have indicated that the oral LD₅₀ of DMHP for rats is 3.05 g per kilogram of body weight and that the minimum lethal dose following application to the skin of rabbits was found to be between 2.4 to 3.1 g per kilogram. Thus, from the standpoint of oral ingestion or skin absorption, DMHP can be considered only slightly toxic.

DMHP has been found to be a skin irritant on prolonged or repeated exposure, and it is painfully irritating to the eyes if splashed into them; but DMHP is no more toxic than many materials which currently comprise components of coating formulations. Normal handling and use precautions should preclude any serious danger to personnel working with this material.

C. Coatings Prepared from ZnO and Organo-Phosphorus Compounds Other than DMHP

The reactions of zinc oxide with organo-phosphorus compounds were studied with the expectation that knowledge of these reactions and the properties of the products formed would shed some light on the nature of the reaction occurring in the ZnO-DMHP mixtures and on the structures of the products of the reaction.

1. ZnO-polyphosphoric acid coating

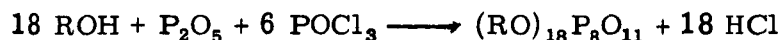
Polyphosphoric acid was prepared by the reaction of equimolar quantities of orthophosphoric acid and phosphorus pentoxide under nitrogen at 225-250° C for 10 hours. The reaction product was a light yellow syrup that was difficultly soluble in water.

Four blends containing 10 parts of polyphosphoric acid and 1, 2, 5, or 10 parts of ZnO were prepared, and attempts were made to form coatings of them on aluminum panels. The reaction products formed hard, brittle, discrete agglomerates; none of them formed a coherent coating on the aluminum. Although coatings were not formed, it was of interest to determine whether the reaction product was similar in heat stability and water solubility to the products formed by the ZnO-DMHP reaction.

A 1-g sample of the reaction product was ground to a fine powder and immersed in approximately 200 ml of water at 60° C for 1 hour. The undissolved portion was filtered off and dried. It was found that 93% of the material was insoluble in water. Some coatings prepared by the ZnO-DMHP-EAP reaction that have been rated as water resistant have contained as little as 83% insoluble material. Heating the ZnO-polyphosphoric acid reaction product at 1000° F for 5 minutes caused a weight loss of 9.3%. This is only slightly more than the usual 3-6% loss that occurs when ZnO-DMHP-EAP coatings that are considered heat stable are similarly heated. Thus, the products produced by the reaction of ZnO with polyphosphoric acid are similar to those produced by the ZnO-DMHP-EAP reaction in thermal stability and water resistance, but not in cohesive properties.

2. ZnO-methyl(ethyl) polyphosphate coatings

The methyl and ethyl esters of polyphosphoric acid were prepared by the method described in U. S. Patent 2, 510, 033. The reaction involved is represented schematically below:



R = alkyl groups containing 2-18 carbon atoms.

The patent does not mention the preparation of the methyl ester; however, the same reaction techniques were used with methyl alcohol as one of the reactants.

The alcohol was added dropwise to a slurry of phosphoric anhydride and dry heptane which was cooled with an ice bath. After all the alcohol was added, the addition of phosphoryl chloride was started; and, simultaneously, a water aspirator pump was used to evacuate the hydrogen chloride gas formed by the reaction. The reaction mixture was stirred continuously, and the temperature was maintained below 40° C. The evolution of gas (HCl) continued for several hours after addition of the phosphoryl chloride was complete, indicating continued reaction. Stirring of the reaction mixture under reduced pressure was continued for several hours after evolution of gas had stopped. Finally, the unreacted alcohol and phosphoryl chloride were removed by distillation under reduced pressure.

In preliminary studies of this system, the best coating was formed by reacting 10 parts of ZnO and 6 parts of the methyl ester of polyphosphoric acid (this amount was barely enough to wet the zinc oxide), and then diluting the reaction product with 6 parts of water and 4 parts of toluene to make a smooth, free-flowing coating mix for application to panels. The reactants were mixed by hand on a glass plate, doctored onto aluminum panels, and cured at laboratory conditions. The coatings prepared in this manner were smooth, well bonded, and heat resistant; but they were soft and not water resistant. Coatings containing greater proportions of the ester were neither heat resistant nor water resistant.

The similarities of properties of the products formed from the reactions of zinc oxide with the polyphosphate esters and with DMHP indicate that formation of a polyphosphate may be one step in the reaction of zinc with DMHP. To further explore this possibility, coatings were prepared from different mole ratios of zinc oxide and methyl polyphosphate, and the coatings were cured under various controlled conditions of temperature and humidity. The ester was mixed with ZnO in mole ratios of 1 to 2,

1 to 1, and 2 to 1, and then 3 parts of toluene and 1 part of ethyl acid phosphate (EAP) for every 10 parts of ZnO were added to each mixture. The EAP was added to accelerate the reaction, and toluene was used as a diluent. The mixtures were mixed thoroughly in a beaker, and then they were doctored onto aluminum panels with a spatula. Within 10 minutes after being doctored onto the aluminum panels, the coated panels were placed in a controlled atmosphere to cure. The conditions of temperature and relative humidity used for curing were 72° F and 60, 75, and 90% relative humidity; 100° F and 40, 55, and 70% relative humidity; 136° F and 20, 35, and 50% relative humidity. All of the curings were carried out under the controlled conditions for 24 hours. Data on the properties of the coatings are given in Table VIII.

The coatings made from the 1 to 2 mole ratio of ester to ZnO were slightly better in hardness and appearance than the others; and the coating obtained under curing conditions of 72° F and 90% relative humidity was resistant to water and heat. When cured at 72° F and 90% relative humidity, the coatings obtained from mole ratios of ester to ZnO of 1 to 1 and 2 to 1 had good heat resistance but poor water resistance. These water- or heat-resistant coatings were not well bonded to the aluminum. All of the other coatings had neither good water resistance nor good heat resistance.

In comparison to ZnO-DMHP coatings, the properties of the coatings obtained by reacting ZnO with methyl polyphosphate were not as good. The ZnO-DMHP coatings generally were hard, good in appearance, and resistant to both water and heat, if prepared under proper conditions. But the ZnO-ester coatings generally were poor in hardness and appearance; and, except in the three experiments mentioned above, they were neither water nor heat resistant. ZnO-DMHP coatings generally become more water resistant and less heat resistant as the relative humidity during curing at a given temperature is increased. The ZnO-ester coatings, however, did not exhibit a characteristic pattern with changes in curing conditions.

From the results of these studies, polyphosphates do not appear to be an intermediate in the formation of coatings by the ZnO-DMHP-EAP reaction.

3. ZnO-dibutylamine phosphite (phosphate) coatings

U. S. Patent 2,952,562 describes air-curable coatings formed by the reaction of di-n-butylamine phosphate with zinc or lead silicates. Presumably, the amine phosphate decomposes slowly to form phosphoric acid and di-n-butylamine, and the phosphoric acid then reacts with the

Table VIII. Properties of Coatings Prepared from Mixtures of Methyl Polyphosphate and Zinc Oxide and Cured Under Various Conditions

Coating composition ^a		Curing conditions ^b		Hardness	Surface	Bonding	Properties of coatings		
Mole ratio, ester to zinc oxide		Temperature, °F	Relative humidity, %				Water resistance	Heat resistance	Bonding after heating
2 to 1		72	60	2	2	3	2	3	-
1 to 1		72	60	2	1	1	3	3	-
1 to 2		72	60	1	1	3	3	3	-
2 to 1		72	75	2	2	3	2	3	-
1 to 1		72	75	2	2	2	3	3	-
1 to 2		72	75	1	1	1	3	3	-
2 to 1		72	90	3	2	3	3	1	3
1 to 1		72	90	3	2	3	3	1	3
1 to 2		72	90	2	2	3	1	1	3
2 to 1		100	40	2	2	1	3	3	-
1 to 1		100	40	2	2	1	3	3	-
1 to 2		100	40	2	1	1	3	2	3
2 to 1		100	55	3	2	1	3	3	-
1 to 1		100	55	2	2	1	3	3	-
1 to 2		100	55	2	1	1	3	3	-
2 to 1		100	70	1	2	1	3	3	-
1 to 1		100	70	1	1	1	3	3	-
1 to 2		100	70	1	1	1	3	3	-
2 to 1		136	20	2	2	1	3	3	-
1 to 1		136	20	2	2	1	3	3	-
1 to 2		136	20	1	2	1	3	3	-
2 to 1		136	35	1	2	1	3	3	-
1 to 1		136	35	1	2	1	3	3	-
1 to 2		136	35	1	2	1	3	3	-
2 to 1		136	50	1	1	3	3	3	-
1 to 1		136	50	1	1	3	3	3	-
1 to 2		136	50	1	1	2	3	3	-

^a All coatings contained 1 part EAP and 3 parts toluene for every 10 parts zinc oxide

^b Cured 24 hours

metal silicate to form a coating. It was reasoned that a similar reaction might take place in the case of ZnO and DMHP; that is, the DMHP might slowly hydrolyze to an acid that reacts with the ZnO. Attempts were made to prepare coatings by the reaction of ZnO and di-n-butylamine phosphate to find out whether this reaction produced the same products as the reaction of ZnO with DMHP.

A sample of di-n-butylamine phosphate was prepared, as described in the patent, by adding reagent grade phosphoric acid slowly to a solution of di-n-butylamine in isopropyl alcohol and a small amount of water. The resulting solution was clear and had a low viscosity.

In some coating experiments, a smooth, thin layer of ZnO was applied to aluminum panels and the di-n-butylamine phosphate solution was sprayed on the ZnO. Other aluminum panels were coated by spreading on the panels mixtures of 10 parts of ZnO with 12, 20, or 40 parts of the amine phosphate solution. All of the coatings were cured 24 hours at laboratory conditions before evaluation.

All the coatings were soft, but they were well bonded to the aluminum. None of the coatings were water resistant, but the coatings prepared from the mixtures containing 20 or 40 parts of the amine phosphate solution were heat resistant, which made them of interest for further study.

Coatings were prepared under a variety of curing conditions from mixtures of ZnO and di-n-butylamine phosphite and from mixtures of ZnO and di-n-butylamine phosphate, and the properties of the coatings were determined. Di-n-butylamine phosphate was investigated to determine whether oxidation of the phosphite to phosphate may be involved in the reaction of di-n-butylamine phosphite and DMHP with ZnO. If oxidation does occur, the phosphite and the phosphate would be expected to give products with significantly different properties.

Samples of di-n-butylamine phosphite and di-n-butylamine phosphate were prepared, as described in the patent above, by adding reagent grade phosphorous or phosphoric acid slowly to a solution of di-n-butylamine in isopropyl alcohol and a small amount of water. ZnO was added to the resulting solutions to give mole ratios of the phosphite or phosphate salt to ZnO of 1 to 1 and 1 to 2. These mixtures were doctored onto aluminum panels, and the coatings were cured under various conditions of temperature and humidity and then were evaluated. Data obtained on coating properties are shown in Tables IX and X.

Table IX. Properties of Coatings Prepared from Mixtures of Zinc Oxide and Di-n-butylamine Phosphite and Cured Under Various Conditions

Coating composition Mole ratio, oxide to di-n-butylamine phosphite	Curing conditions ^a		Properties of coatings			
	Temperature, °F	Relative humidity, %	Hardness	Surface Bonding	Water resistance	Heat resistance
1 to 1	72	60	2	1	3	3
2 to 1	72	60	2	2	3	3
1 to 1	72	75	2	1	1	1
2 to 1	72	75	3	2	3	3
1 to 1	72	90	3	2	3	1
2 to 1	72	90	3	2	3	1
1 to 1	100	40	1	2	3	2
2 to 1	100	40	3	2	3	3
1 to 1	100	55	1	1	2	1
2 to 1	100	55	2	1	3	1
1 to 1	100	70	2	1	2	3
2 to 1	100	70	2	1	3	3
1 to 1	136	20	1	1	1	1
2 to 1	136	20	2	1	2	2
1 to 1	136	35	1	1	1	2
2 to 1	136	35	2	1	2	2
1 to 1	136	50	2	1	1	1
2 to 1	136	50	2	2	2	1

^aCured 24 hours

Table X. Properties of Coatings Prepared from Mixtures of Zinc Oxide and Di-n-butylamine Phosphate and Cured Under Various Conditions

Coating composition Mole ratio, oxide to di-n-butylamine phosphate	Curing conditions ^a		Properties of coatings			
	Temperature, °F	Relative humidity, %	Hardness	Surface	Bonding	Water resistance
1 to 1	72	60	1	1	1	3
2 to 1	72	60	1	1	1	3
1 to 1	72	75	1	1	1	3
2 to 1	72	75	2	1	1	1
1 to 1	72	90	3	1	3	3
2 to 1	72	90	3	2	3	3
1 to 1	100	40	1	1	1	3
2 to 1	100	40	1	1	1	3
1 to 1	100	55	1	1	1	2
2 to 1	100	55	2	1	1	2
1 to 1	100	70	1	1	2	3
2 to 1	100	70	2	1	3	3
1 to 1	136	20	1	1	1	2
2 to 1	136	20	2	1	1	1
1 to 1	136	35	1	1	1	1
2 to 1	136	35	2	1	3	3
1 to 1	136	50	2	1	2	1
2 to 1	136	50	2	1	3	1

^aCured for 24 hours

The results of these studies were encouraging. Hard coatings with good surface appearances were obtained that were heat and water resistant and well bonded to the aluminum.

With the coatings prepared from the mixtures of 1 mole of ZnO with 1 mole of di-n-butylamine phosphite, three of the nine curing conditions studied gave coatings with good heat and water resistance. The other six curing conditions studied gave coatings with poor heat resistance, poor water resistance, or both. None of the cured coatings prepared from the mixtures of 2 moles of ZnO and 1 mole of di-n-butylamine phosphite were water resistant, but four of them did have good heat resistance.

With the coatings prepared from the mixture of 2 moles of ZnO and 1 mole of di-n-butylamine phosphate, three of the curing conditions studied gave coatings with good heat and water resistance. All of the curing conditions studied gave heat-resistant coatings with this mixture. For the coatings prepared from the mixture of 1 mole of ZnO and 1 mole of di-n-butylamine phosphate, five of the nine curing conditions studied gave heat-resistant coatings, and one of these curing conditions also gave a water-resistant coating.

In general, the highest curing temperature (136° F) resulted in coatings with higher heat and water resistance. For example, when cured at 72° F, ten of the twelve coatings prepared had poor properties, whereas at 136° F, ten of the coatings had fair or good properties. At a given curing temperature, there was no apparent trend between properties of the coatings and the relative humidity of curing.

The results are not sufficiently consistent to lead to any firm conclusions, but some interesting inferences are possible. The formation of ZnO-amine phosphite (phosphate) coatings with properties that vary with curing conditions makes it probable that the reactions involved in the formation of the coatings are similar to those involved in the formation of the ZnO-DMHP coatings: hydrolysis of the organo-phosphorus compounds to acids that react with the ZnO. The observation that the phosphite and the phosphate yielded about the same types of coatings indicates that oxidation of the phosphite is not a major factor in determining the quality of the coatings, except for a possibility that it affects the heat resistance.

There seems to be no explanation of the fact that good coatings were obtained from the amine salts at 136° F, whereas with DMHP, all coatings cured at this temperature were deficient in either heat resistance or water resistance.

D. Coatings Prepared from DMHP and Metal Oxides Other than ZnO

1. Lithia and beryllia

During the previous contracts, preliminary studies were made of the reactions of lithia with organo-phosphorus compounds, such as DMHP, EAP, monoethyl acid orthophosphate, and diethyl hydrogen phosphite, for making coatings. The best coating obtained in these studies was hard, well bonded, and heat resistant; but it was also water soluble. During this report period, coatings were made by the reaction of a mixture of DMHP and EAP, with mixtures of lithia or beryllia and the oxide of one of the following materials: zinc, zirconium, titanium, magnesium, calcium, or bismuth. The ratio of DMHP:EAP:metal oxide (total) in all of the mixtures was 12:1:10. The coatings were doctored onto aluminum panels and cured at 72° F and 75% relative humidity for 24 hours. These are the curing conditions that have been used to prepare the ZnO-DMHP-Ludox LS coatings having both heat and water resistance. The blends prepared and the data obtained on coating properties are shown in Table XI.

It was hoped that the lithia or beryllia would impart heat resistance to the coatings and that the other oxides would impart water resistance. All of the coatings were heat resistant, but only the one containing 9 parts of zinc oxide, 1 part of beryllia, 12 parts of DMHP, and 1 part of EAP was also water resistant. This coating was hard and smooth but slightly poorer in bonding than the best coatings developed previously. Only 2 out of the 18 coatings were hard; both of these contained beryllia. The bonding of coatings containing beryllia to the substrate was slightly better than the bonding of coatings containing lithia. In trials that are not listed in Table I, it was found that mixtures of oxides containing more than about 25% of lithia were too reactive and produced blends that had too short a pot life to be made into coatings.

Although the one coating of interest formed in this study was primarily a zinc oxide system, further work with zinc oxide-beryllia combinations may be of value.

2. Ceramic frits

Experiments conducted during the previous contract period indicated some promise for ceramic frits as components of heat-resistant coatings. Boron oxide frits containing high percentages of zinc oxide, magnesium oxide, barium oxide, or phosphorus were selected for further study on the basis of the results of the earlier work. The compositions of the frits prepared for the further studies are shown in Table XII.

Table XI. Properties of Coatings Made from Combinations of DMHP and EAP with Lithia or Beryllia and Other Metal Oxides

DMHP	EAP	Coating composition, parts by weight							Ratings after curing ^a					
		BeO	Li ₂ O	ZnO	ZrO ₂	TiO ₂	MgO	CaO	BiO ₂	Hardness	Surface	Bonding	Water resistance	Heat resistance
12	1	1	-	9	-	-	-	-	-	1	1	2	1	1
12	1	5	-	-	-	-	-	5	-	1	1	1	3	1
12	1	1	-	-	-	-	-	9	-	3	1	1	3	1
12	1	2.5	-	-	7.5	-	-	-	-	3	1	3	3	1
12	1	2.5	-	-	-	7.5	-	-	-	3	1	2	3	1
12	1	5	-	-	-	5	-	-	-	3	1	2	3	1
12	1	7.5	-	-	2.5	-	-	-	-	3	1	2	3	1
12	1	7.5	-	-	-	2.5	-	-	-	3	1	2	3	1
12	1	1	-	-	-	-	9	-	-	3	1	2	3	1
12	1	5	-	-	-	-	5	-	-	3	1	2	3	1
12	1	1	-	-	-	-	-	-	9	3	1	3	3	1
12	1	5	-	-	-	-	-	-	5	3	1	3	3	1
12	1	-	1	9	-	-	-	-	-	3	1	3	3	1
12	1	-	2.5	-	7.5	-	-	-	-	3	1	3	3	1
12	1	-	2.5	-	-	7.5	-	-	-	3	1	3	3	1
12	1	-	1	-	-	-	9	-	-	3	1	3	3	1
12	1	-	1	-	-	-	-	9	-	3	1	3	3	1
12	1	-	1	-	-	-	-	-	9	3	1	3	3	1
12	1	-	1	-	-	-	-	-	9	3	1	3	3	1

^aAll coatings were cured at 72°F and 75% RH for 24 hours

Table XII. Compositions of Frits

Frit 2859-49

Boron oxide	750 g
Zinc oxide	600 g
Barium oxide	150 g

Frit 2859-50

Boron oxide	525 g
Sodium hydroxide	546 g
Magnesium carbonate	1160 g

Frit 2859-51

Boron oxide	510 g
Barium oxide	570 g
Sodium hydroxide	546 g

Frit 2859-52

Boron oxide	510 g
Zinc phosphate, tribasic	570 g
Sodium hydroxide	546 g

The frits were prepared by thoroughly mixing the various components listed in Table XII in a ball mill. Each mixture was placed in a clay crucible and the crucible was placed in a gas-air furnace which had been preheated to approximately 1600° F. The furnace temperature was slowly raised to 2000° F over a period of about one hour and held there for approximately 30 minutes. The melt was solidified and cooled by pouring it slowly into cold water. The solid product was dried and then ball milled for 24 hours. The ball-milled material was screened and the portion passing through a 270-mesh sieve was used in coating formulations.

The frits containing the zinc oxide (2859-49), the magnesium oxide (2859-50), and the barium oxide (2859-51) were each evaluated in two formulations. One formulation contained 10 parts of frit, 5 parts of DMHP, and 1 part of EAP; the other, 10 parts of frit and 5 parts of EAP. The 5 parts of DMHP or EAP in the formulations was the approximate theoretical amount required to react with the active metal oxides.

The frit containing the phosphorus (2859-52) was evaluated in three formulations. One contained 10 parts of frit and 5 parts of EAP; one contained 10 parts of frit and 6 parts of water; and one contained 10 parts of frit, 5 parts of water, and 2 parts of EAP. Water was used in two of the formulations because the phosphorus present in the frit may have been present as phosphorus pentoxide, which might react with water to form coatings but might not react with EAP. The amount of water used was just enough to give the formulation a coating consistency.

The coatings were mixed and applied to aluminum panels and cured for 24 hours at 72° F and 75% relative humidity. The compositions of the mixtures that were prepared and the properties of the coating they produced are given in Table XIII. The data show that Frit 2859-50 formed a hard, reasonably well-bonded, heat-resistant, water-resistant coating similar to the ZnO-DMHP-Ludox LS coating. Frit 2859-49 formed coatings that either were not heat resistant, were poorly bonded, or both. The other two frits (2859-51 and 2859-52) formed coatings that were soft, poorly bonded, and neither heat nor water resistant.

Because a heat-resistant, water-resistant coating was obtained with Frit 2859-50, some further work with this frit would be of interest.

E. Coatings Prepared from Mixtures of ZnO, DMHP, and Refractory Metals

Refractory metals have been used to improve the heat resistance of ceramic coatings that are cured by heating. To determine whether they would also improve the heat resistance of the air-cured coatings being developed, a series of coatings containing small amounts of refractory metals were prepared and evaluated. The refractory metals studied were zirconium, aluminum, and titanium. Coating mixtures were prepared containing 0.5 or 1.0 part of the refractory metal powder (-325 mesh), 10 parts of zinc oxide, and 12 parts of DMHP. Water and EAP were not used in the formulations since both of these materials react with the refractory metals too rapidly or they form undesirable side products. The coatings were cured at 72° F and 75% relative humidity for 24 hours. The compositions used and the results obtained are given in Table XIV.

Table XIII. Properties of Coatings Made with Glassy Frits

		Coating composition, parts by weight				Ratings after curing ^a			
DMHP	EAP	Frit	Frit	Frit	Frit	Hardness	Surface	Bonding	Water resistance
		2859-49	2859-50	2859-51	2859-52				
5	1	10	-	-	-	1	1	3	3
-	5	10	-	-	-	1	1	2	2
5	1	-	10	-	-	1	1	2	1
-	5	-	10	-	-				
5	1	-	-	10	-	3	1	3	3
-	5	-	-	10	-	3	2	3	3
-	5	-	-	-	10	3	2	3	3
-	-	-	-	-	10	3	1	3	3
-	2	-	-	-	10	3	1	3	2

Too Reactive

^aAll coatings were cured at 72°F and 75% RH for 24 hours

Table XIV. Properties of Coatings Made from Mixtures of ZnO, DMHP, and Refractory Metals

Coating composition, parts by weight					Ratings after curing ^a				
ZnO	DMHP	Ti	Zr	Al	Hardness	Surface	Bonding	Water resistance	Heat resistance
10	12	0.5	-	-	1	2	3	3	2
10	12	1.0	-	-	1	2	3	3	2
10	12	-	0.5	-	1	2	3	3	3
10	12	-	1.0	-	1	2	3	3	3
10	12	-	-	0.5	1	1	3	2	3
10	12	-	-	1.0	1	1	3	1	3

^a All coatings were cured at 72° F and 75% relative humidity for 24 hours.

None of the coatings formed was heat resistant, and only the one containing one part of aluminum was water resistant. Because of these results, no further work with refractory metals is planned.

VI. RECOMMENDATIONS

The properties of the coating developed in this research program make it of interest for protecting metal surfaces that are exposed to temperatures up to about 1000° F and to weathering. Although the moisture conditions required for curing the coatings at low temperatures would make application of the coatings to large structures in outdoor areas difficult, the conditions for applying the coatings are feasible for treating smaller metal articles that can be processed in small or moderate size enclosed spaces. It is recommended that coatings of the zinc oxide, dimethyl hydrogen phosphite, colloidal silica paint developed in this program be more fully evaluated to determine the protection that they can provide various metals under a wide range of conditions of exposure.

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